

REMARKS

Entry of the foregoing amendments to the application is requested on the grounds that the claims, as amended, patentably distinguish over the cited art of record or, alternatively, place the application in better condition for appeal. The claims more particularly point out and distinctly claim the subject matter which Applicants regard as the invention. No new issues have been added which would require further consideration and/or search, nor has any new matter been added. The claims as amended are believed to avoid the rejections applied in the Final Office Action for reasons set forth more fully below.

The Final Office Action of November 10, 2008 has been received and carefully reviewed. It is submitted that, by this Amendment, all bases of rejection are traversed and overcome. Upon entry of this Amendment, claims 1-20, 48, 49 and 68-72 remain in the application. Claims 5 and 7-11 have been withdrawn. Reconsideration of the claims is respectfully requested.

Telephonic Interview

At the outset, Applicants' below-listed Attorney would like to sincerely thank Examiner O'Neill for all the time and courtesies extended during the telephonic interview of January 7, 2009. During the interview, the differences between nanowires and nanoparticles were discussed, and claim 1 (in particular, the patterned film) was discussed in light of the references of record. A proposed amendment to claim 1 was discussed, which included further defining the patterned film to include the imaged photoresist.

Withdrawn Claims

Applicants respectfully submit that claim 1 is an allowable generic claim, and that claims 5 and 7-11 (directed to a withdrawn species) should be considered allowable. As such, it is submitted that currently withdrawn claims 5 and 7-11 are entitled to consideration.

Rejections under 35 U.S.C. § 112, second paragraph

Claims 1-4, 6, 12-20, 48, 49 and 68-72 stand rejected under 35 U.S.C. § 112, second paragraph for failing to particularly point out and distinctly claim the subject matter which the Applicants regard as the invention. The Examiner states that the limitation “including insoluble matter of a liquid” is unclear because there is no indication of what type of liquid is being used or when/how the liquid is being used in the product. The Examiner also states that the term “insoluble matter” is not defined by the claims, and that the specification does not provide a standard for ascertaining the requisite degree. Furthermore, the Examiner points out that the claims omit essential steps. More particularly, the Examiner states that, “the missing elements are: the process or steps in which the liquid is washed away with the nanowires, leaving insoluble matter...” (see the instant Final Office Action at page 3).

Applicants strongly disagree with all of the rejections set forth under 35 U.S.C. § 112, second paragraph. However, in order to expedite prosecution, the Applicants have amended independent claims 1, 48 and 49 to further clarify that the patterned film includes insoluble matter of an imaged photoresist having a plurality of nanowires dispersed therein. Support for this recitation may be found throughout the specification as filed, at least at page 7, lines 12-24, which clearly sets forth that the liquid used to provide the insoluble matter is a photoresist that is exposed to UV imaging.

Applicants submit that examples of positive and negative photoresists are provided in the specification as filed, at page 4, lines 3-16. As such, it is submitted that the Applicants’ revised claims and the specification as filed provides one skilled in the art with the type of liquid being used in the patterned film.

It is further submitted that one skilled in the art would be cognizant of the fact that negative photoresists are materials that become insoluble in developing solutions when exposed to optical radiation, and that positive photoresists are materials that become soluble in developing solution when exposed to optical radiation (see, e.g., Exhibit A, second paragraph of “Introduction”, filed concurrently herewith). In view of this knowledge, it is further submitted that one skilled in the art would understand that, in some instances, the “insoluble matter” will be the portion of the negative photoresist that is

exposed to light, and, in other instances, the “insoluble matter” will be the portion of the positive photoresist that is not exposed to light.

As such, in light of the Applicants’ application as filed and the knowledge of one skilled in the art at the time the invention was made, it is submitted that one skilled in the art would understand that the insoluble matter of the imaged photoresist in the patterned film will depend upon whether the photoresist used to form the patterned film is a positive or a negative photoresist. Furthermore, from the examples provided in the specification as filed, it is further submitted that one skilled in the art could readily ascertain how to achieve the patterned film including the desirable insoluble matter.

Finally, Applicants submit that currently pending independent claims 1 and 49 are directed to fuel cells (not methods), and that claim 48 is directed to a method of using a fuel cell which is equivalent to the fuel cell of claim 1. These claims are not missing “essential steps.” More particularly, the patterned film of Applicants’ independent claims includes insoluble matter of an imaged photoresist having a plurality of nanowires dispersed therein. In her argument, the Examiner refers to the liquid that is washed away as being a missing element (see Page 3 of the Final Office Action dated November 10, 2008). However, the Applicants submit that such soluble liquid is **not** part of the resulting patterned film, and thus is not a missing element in the claims recited by the Applicants.

For all the reasons stated above, Applicants submit that the rejections of claims 1-4, 6, 12-20, 48, 49 and 68-72 under 35 U.S.C. § 112, second paragraph are erroneously based and/or have been traversed and overcome, and withdrawal of the same is respectfully requested.

Rejections under 35 U.S.C. § 102(b)

Claims 1-4, 6, 12, 13, 15-20, 48, 49 and 68-71 stand rejected under 35 U.S.C. § 102(b) as being anticipated by Seabaugh et al. (U.S. Patent Application Publication No. 2003/0027033). The Examiner states that Seabaugh discloses a solid oxide fuel cell including a ceramic electrode upon an electrolyte substrate. The ceramic electrode includes a mixture of two or more components including ionically conducting ceramic electrolyte material and an electrode material powder. The Examiner asserts that the

ceramic electrode is “inherently patterned”. In response to the Applicants’ arguments filed July 28, 2008, the Examiner indicates that “[b]ecause Seabaugh et al. discloses the nanoparticles being on the nano-scale, the disclosed nanoparticles could still be considered nanowires since the term ‘dimension’ is used. ‘Dimension’ encompasses ‘length’, which would correspond to the dimensions of a nanowire.”

At the outset, Applicants have amended independent claims 1, 48 and 49 to recite that the patterned film includes an insoluble portion of an imaged photoresist and nanowires dispersed therein.

Seabaugh does not teach or suggest the use of a photoresist in his composites, and thus it is submitted that, for at least this reason, the 35 U.S.C. § 102(b) rejection of claims 1-4, 6, 12, 13, 15-20, 48, 49 and 68-71 should be withdrawn.

Additionally, Applicants strongly disagree with the Examiner’s conclusions regarding Seabaugh’s nanoparticles. Seabaugh specifically teaches the formation of composites formed with two different powders (see, e.g., Figs. 3, 4, and 6), and that the powder mixtures are on the nanoscale (i.e., less than 100 nm in dimension, see paragraph [0009]).

A powder is defined as “matter in a finely divided state” or “a preparation in the form of fine particles” (see Merriam Webster’s Collegiate Dictionary, Tenth Edition, 1996). As mentioned hereinabove, Seabaugh specifically teaches the use of powders (i.e., particles) on the nanoscale, or less than 100 nm in dimension (see paragraph [0009] of Seabaugh). Since Seabaugh does not specifically note that the particles are less than 100 nm in one dimension (i.e., indicating that the particles have more than one dimension), one skilled in the art would glean from this teaching (i.e., “less than 100 nm in dimension”) that the powder particles of Seabaugh have a single dimension (i.e., diameter) that is less than 100 nm.

In sharp contrast, Applicants’ patterned film includes nanowires. The definition of a nanowire is, “a wire of material, the diameter of which is less than 100 nm” (see, www.nature.com/nrd/journal/v2/n1/glossary/nrd988_glossary.html). It is submitted that one skilled in the art would be cognizant of the fact that wires have 1 dimension (i.e., length) that is longer than another dimension (i.e., diameter). If wires had a single

dimension, as suggested by the Examiner, the wire would be a particle, NOT a wire. Applicants have provided examples of both lengths and diameters of their nanowires (see, e.g., page 9, lines 19-27, and originally filed claims 16-19). It is submitted that since one skilled in the art knows that the length of a nanowire is larger than its width, the exemplary lengths and widths provided by the Applicants would be selected to achieve the described nanowires. Furthermore, Applicants' own Fig. 3 schematically illustrates the differences between nanowires 14 and nanoparticles 22.

In light of the above discussion, nanoparticles are different from nanowires in structure and in the synthesis thereof. For example, a nanowire has an aspect ratio that is greater than an aspect ratio of a nanoparticle, at least in part because a nanowire has a different length and width, and a nanoparticle has a diameter. Furthermore, nanowires are significantly more challenging to manufacture than spherical structured nanoparticles. Still further, the surface area afforded by a nanoparticle is much less than the surface area afforded by a nanowire.

As the nanoparticles of Seabaugh are NOT nanowires, and nanowires are, in fact, very different from nanoparticles, it is submitted that Seabaugh neither anticipates nor renders obvious the use of nanowires in his ceramic electrode.

The Applicants also respectfully disagree with the Examiner in her conclusion that Seabaugh teaches that the ceramic electrode is an inherently patterned film, **as the term "patterned film" is defined by the Applicants**. The Examiner states that the process by which the Applicants' patterned film is established is not given patentable weight. Applicants would like to point out that they are not arguing that the patterning process itself is patentable, but rather that the patterned film resulting from this process is patentable.

On page 7 of Applicants' specification as filed, the patterning process is described. This process results in the patterned film recited in Applicants' independent claims 1, 48 and 49, which includes, in addition to the nanowires, any insoluble matter of an imaged photoresist (which remains after the patterning process is complete).

Such a patterned film is not taught or even suggested by Seabaugh. Seabaugh teaches that his ceramic electrode includes ceramic electrolyte materials (i.e., powders)

and ceramic electrode materials (i.e., powders). Seabaugh also teaches that this mixture may be an electrode coating or an electrode substrate (see paragraph [0020]). When describing how the mixture is established, Seabaugh explains that inks are prepared with commercial terpinol-based ink vehicle and “circular patterns...were deposited by screen printing...” (see Examples 20-25). These inks, and the methods by which they are established, do not result in a patterned film *as the phrase is defined by the Applicants*. The inks of Seabaugh form a coating, which includes the ink vehicle and the powder mixture, on the particular substrate in a pattern defined by the printing process. In sharp contrast, Applicants’ patterned film includes the insoluble matter of the imaged photoresist and the nanowires (as recited in Applicants’ independent claims) established in a pattern defined by an imaging process.

Applicants are not arguing that Seabaugh’s ceramic electrode is not patterned. Rather, Applicants are arguing that Seabaugh’s ceramic electrode is not the “patterned film” defined by the Applicants and as recited in Applicants’ claims. As set forth hereinabove, Seabaugh’s electrode is not the same as Applicants’ **patterned film**, which as a result of Applicants’ patterning process, includes insoluble matter of an imaged photoresists and nanowires.

For all the reasons stated above (and for those reasons provided hereinbelow in reference to the § 103(a) rejection of original claim 72, the subject matter of which has been incorporated into claim 1), it is submitted that Applicants’ invention as defined in independent claims 1, 48 and 49, and in those claims depending ultimately therefrom, is not anticipated, taught or rendered obvious by Seabaugh, either alone or in combination, and patentably defines over the art of record.

Claims 1-3, 6, 12-16, 18-20, 48, 49 and 68-71 stand rejected under 35 U.S.C. § 102(b) as being anticipated by Huang et al. (U.S. Patent Application Publication No. 2002/0098406). The Examiner states that Huang discloses a solid oxide fuel cell including an electrolyte substrate and an electrode including a paste of nano-sized particles of electrocatalytic noble metals and ceramic ionic conducting particles. The Examiner asserts that the paste is “inherently patterned”.

As previously mentioned, Applicants have amended independent claims 1, 48 and 49 to recite that the patterned film includes an insoluble portion of an imaged photoresist and nanowires dispersed therein.

Huang does not teach or suggest the use of a photoresist in his anode, and thus it is submitted that, for at least this reason, the 35 U.S.C. § 102(b) rejection of claims 1-4, 6, 12, 13, 15-20, 48, 49 and 68-71 should be withdrawn.

Furthermore, the Applicants again point out that their patterned film includes nanowires. In sharp contrast, Huang teaches the use of nanoparticles in his paste. In light of the above discussion regarding the differences between nanowires and nanoparticles, it is submitted that Huang neither anticipates nor renders obvious the use of nanowires.

The Applicants also respectfully disagree with the Examiner's conclusion that the Huang electrode is "inherently patterned", as the term "patterned" is defined by the Applicants. Huang teaches that his electrode includes a three-dimensional solid phase having an electrocatalytic noble metal phase of noble metal particles and an ion conducting phase of ionic conductor particles. Huang teaches that an electrode paste is formulated, including the particle mixture and a solvent which is compatible with screen printing, tape casting, slip casting, vapor deposition, or thermal spraying (see paragraph [0050]). The paste of Huang is deposited to form a coating, which includes the solvent and the particle mixture, on the electrolyte substrate in a pattern defined by one of the listed deposition techniques. In sharp contrast, Applicants' patterned film includes the insoluble matter of an imaged photoresist and the nanowires in a pattern defined by an imaging process.

For all the reasons stated above, it is submitted that Applicants' invention as defined in independent claims 1, 48 and 49, and in those claims depending ultimately therefrom, is not anticipated, taught or rendered obvious by Huang, either alone or in combination, and patentably defines over the art of record.

Rejections under 35 U.S.C. § 103(a)

Claim 72 stands rejected under 35 U.S.C. § 103(a) as being unpatentable over Seabaugh as applied to claims 1-4, 6, 12, 13, 15-20, 48, 49 and 68-71 above, and further in view of Monty et al. (U.S. Patent No. 6, 849,911). The Examiner admits that Seabaugh does not disclose "wherein the liquid is a photoresist." The Examiner explains that Monty discloses a method for making electrodes in which nanowires can be grown on a substrate, where a photoresist is spin-coated on the top of the substrate. The Examiner points out that the photoresist is later removed to reveal the isolated nanowires that are present on the substrate. The Examiner concludes that it would have been obvious to use a photoresist as the liquid in the patterned film of Seabaugh because Monty teaches that a photoresist is used to create a pattern in a substrate material.

Claim 72 has been amended to recite that the imaged photoresist of claim 1 is selected from a positive photoresist or a negative photoresist. Support for this revision may be found at page 4, lines 3-7 of the specification as filed.

At the outset, the Applicants reiterate all of the arguments previously made regarding Seabaugh. Applicants further submit that because claim 72 depends from claim 1, claim 72 is allowable for at least the same reasons set forth for the patentability of claim 1.

Applicants further submit that all of the pending claims are also patentable over Seabaugh in view of Monty, at least because Monty does not supply the deficiencies of Seabaugh. In view of the teachings on Monty, it is submitted that one skilled in the art i) would not be led to combine Monty's photoresist with Seabaugh's electrode, and ii) would not achieve the fuel cell recited in Applicants' claim 1 (from which claim 72 depends) even if such a combination were made.

Seabaugh specifically teaches a composite of two different powders. When applying the composite to a substrate, Seabaugh teaches adding the powder mixture to an ink vehicle to facilitate deposition of the powder mixture on the substrate. After deposition, the coating is annealed.

Monty, at Col. 3, line 40 Col. 4, line 11 recites, in part:

...a 200-600 nm thick layer of silicon dioxide (SiO_2) 102 is plasma deposited on top of the base Si substrate 101. On top of this, Ti is thermally evaporated and condensed onto the surface such that a 10-100 nm (e.g., 50 nm) Ti film 103 resides on top of the SiO_2 (note that in other embodiments Ti is sputtered or electron-beam evaporated onto the surface). A 1-5 μm (e.g., about 1 μm) Shipley AZ photoresist (PR) layer 104 is spin-coated onto the Ti film 103 using a spin coater operating at about 1000-5000 RPM. A subsequent baking process is used to remove the solvent. A photomask (essentially a glass plate with a photo-opaque design on it) is applied to the PR layer 104 and is exposed to UV light (e.g., generated by a mercury arc lamp or other source). The photomask is removed and the substrate is placed in a developer which removes the UV-exposed regions or the PR layer 104, thus creating a pattern in the PR layer 104. In Step 1002, the Ti layer 103 is etched using a reactive ion etching (RIE) plasma using a fluorine- or chlorine-containing gas (or other suitable etching process). This generates nanoscale "walls" (nanowalls) of Ti 105 which can then be electrically-biased such that Pd is electrochemically deposited (from a solution) along the Ti walls 105 as Pd nanowires 106 having diameters generally in the range of about 100 nm to about 700 nm, and perhaps smaller. Methods for electrochemically depositing Pd from solution are well known in the art.... In Step 1003, the **patterned photoresist 104 and the Ti walls 105 are removed to reveal the isolated nanowires 106**. (Emphasis added).

Monty is teaching that a photoresist is used to form a pattern for subsequently etching an underlying metal layer to create walls in the underlying metal layer. Such walls are used for subsequent nanowire formation. The exposure of the photoresist layer to UV and a developer creates a pattern in the photoresist layer because the UV exposed regions are removed. However, after creation of the nanowires on the walls, Monty teaches that the remaining photoresist layer (i.e., the insoluble portion) is ALSO REMOVED. Monty does not teach generating a patterned film which includes the insoluble photoresist material, rather he teaches the use of a photoresist as a mask for etching layers underlying the photoresist.

Since Monty's photoresist is essentially a masking layer for etching underlying materials, and **all of the photoresist is ultimately removed**, Applicants submit that one skilled in the art would not be led to replace Seabaugh's ink vehicle with Monty's photoresist.

Furthermore, assuming *arguendo* that one skilled in the art were to include Monty's photoresist with Seabaugh's composite, based on the teachings of Monty, it is submitted that the photoresist would be removed from the composite. As such, any electrode resulting from the combination of Monty and Seabaugh would not be the same as Applicants' patterned film, at least because the insoluble matter would not be present in the electrode.

For all the reasons stated above, it is submitted that Applicants' invention as defined in any of the independent claims, and in those claims depending therefrom, is not anticipated, taught or rendered obvious by Seabaugh and Monty, either alone or in combination, and patentably defines over the art of record.

In summary, claims 1-20, 48, 49 and 68-72 remain in the application. It is submitted that, through this Amendment, Applicants' invention as set forth in these claims is now in a condition suitable for allowance.

Further and favorable consideration is requested. If the Examiner believes it would expedite prosecution of the above-identified application, the Examiner is cordially invited to contact Applicants' Attorney at the below-listed telephone number.

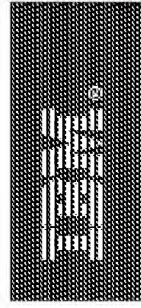
Respectfully submitted,

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Optical lithography

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Negative photoresists for optical lithography

by J. M. Shaw, J. D. Gelorme, N. C. LaBianca, W. E. Conley, and S. J. Holmes

Negative photoresists are materials that become insoluble in developing solutions when exposed to optical radiation. They were the first systems used to pattern semiconductor devices, and still comprise the largest segment of the photoresist industry because they are widely used to define the circuitry in printed wiring boards. However, the current use of negative resists in the semiconductor industry has been limited by past difficulties in achieving high-resolution patterns. Recent advances in the chemistry of negative-resist systems, however, have provided materials with wide processing latitude and high resolution that are used to manufacture IBM's advanced CMOS devices and to achieve high-aspect-ratio patterns for micromachining applications. This paper provides an overview of the history and chemistry of negative-resist systems and their development in IBM.

1. Introduction

The majority of polymers, when exposed to ultraviolet light in the range from 200 to 300 nm (24 eV to 6 eV), form "radical species" which can result in cross-linking, increased molecular weight, insolubilization, and film embrittlement. While industries such as the automotive and aerospace have concentrated research activities on inhibiting these reactions to extend the life of plastic coatings and components, the semiconductor industry has used this effect to its advantage to produce polymeric stencils resistant to the acids and bases used to fabricate semiconductor devices and circuitry. As shown in [Figure 1](#), these photosensitive films, which become insoluble in solvents or water-based developers upon exposure to radiation, form "negative" patterns which are used as temporary stencils to delineate many levels of circuitry in semiconductor devices and printed wiring boards (PWBs). This insolubilization can be achieved by using materials which upon UV exposure either 1) increase in molecular weight, or 2) are photochemically rearranged to form new insoluble products. To increase molecular weight, photoinitiators are generally used that can generate free radicals or strong acids to facilitate polymeric cross-linking or the photopolymerization of monomeric or oligomeric species. Without an increase in molecular weight, negative patterns can be achieved by the photochemical formation of hydrophobic or hydrophilic groups which provide preferential

solubility between the exposed and unexposed resist film.

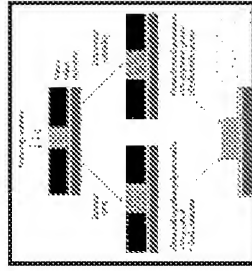


Figure 1

Over the past thirty years, chemists and engineers have been able to provide a wide variety of resists, both negative (insolubilize upon exposure to radiation) and positive (solubilize upon exposure to radiation) to answer the needs of a growing industry. As seen in *Figure 2*, negative resists currently comprise the largest segment of the photoresist market. The choice of whether to use a negative or a positive resist system depends upon the needs of the specific application such as resolution, ease of processing, and cost. Negative resists continue to dominate the fabrication of printed wiring boards, where manufacturing throughput and cost are paramount issues. Positive resists are largely used for the patterning of high-resolution semiconductor devices, although advances in the resolution capability of some negative systems, and the advantage of patterning them on certain device levels, have generated increased interest and usage. A negative resist, because of its wider processing latitude and high resolution, is currently used to pattern critical levels of IBM's advanced CMOS logic devices, where the control of linewidth and its variation across the chip is key to performance. This paper provides an overview of negative resists, including a description of recent work on advanced systems for the fabrication of semiconductors, and the micromachining of microelectromechanical devices (MEMs).

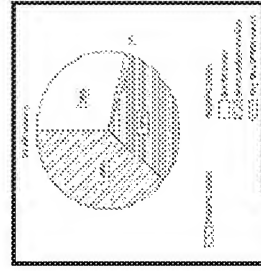


Figure 2

2. Negative photoresists for semiconductors and PWBs

Free-radical-initiated resist systems

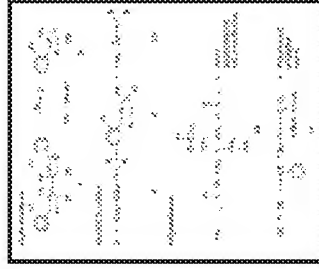
The first negative resists designed specifically to address the growing needs of the semiconductor industry were introduced in the 1960s and were based upon *free-radical-*

initiated photocross-linking or photopolymerization processes. The newly developed lithography tools for the semiconductor industry used the output of mercury arc lamps in the "near UV" at wavelengths from 365 nm to 436 nm; they required a photosensitive system that would be able to form pinhole-free thin films that were resistant to the acids and bases used to pattern devices, with adhesion to unique semiconductor surfaces and metals. Kodak introduced a system called KTR consisting of a bis-aryldiazide photosensitive cross-linking agent which absorbed in the near UV, with a polyisoprene cyclized polymer to provide the necessary film-forming and adhesion properties [1]. As seen in Formula 1, upon exposure the resist cross-links through a free-radical mechanism where nitrene is inserted into the polymeric backbone [2], and the unexposed film is removed using aromatic solvents as developing solutions. However, this resist has several disadvantages: 1) The presence of oxygen acts as a free-radical scavenger, inhibiting cross-linking, and the resist must be exposed under vacuum or nitrogen; 2) the solvent developer swells the cross-linked negative image, causing degradation of the pattern and limiting resolution to 2 μm in a 1- μm -thick coating; and 3) the aromatic solvent developer may pose environmental, health, and safety concerns. This system met semiconductor manufacturing requirements until the mid-1970s, when the demand for increased circuit density generated a need to provide a better photoresist, although similar systems are still used for less demanding applications.



Formula 1

However, for the fabrication of printed wiring boards where resolution requirements are less severe, free-radical photopolymerization provides low-cost, highly sensitive systems that are the mainstay of the industry. Dry-film photoresists, introduced by DuPont in 1968 [3], are the most widely used. They consist of a photopolymerizable layer that is sandwiched between a polyester support film and a separator sheet. This dry film has a number of advantages. After removal of the separator sheet, the dry film is laminated to the substrate and (unlike liquid resists) can bridge or "tent" over the plated-through holes in PWBs. Also, the polyester cover sheet protects the resist film from oxygen diffusion, which would inhibit the cross-linking reaction. Throughout the 1970s these resist systems were developed in chlorinated solvents, but aqueous-base-developable systems are now available [4, 5]. A typical dry-film resist system is shown in Formula 2 and described in detail in Reference [5]. It comprises 1) an initiator which absorbs radiation, forming an imidazole radical (Ia) which abstracts hydrogen from a tertiary amine to form a radical (IIa) which initiates the polymerization process; 2) polyfunctional photopolymerizable monomers (II), which react to form a highly cross-linked, chemically resistant structure; and 3) a binder to provide toughness and film-forming properties, typically a styrene/maleic acid polymer (IV). To meet the ever-increasing wiring density demands, the resolution capability of these materials has steadily improved from 200- μm circuit line dimensions in the 1970s to a current capability of <75 μm .



Formula II

Positive-resist modifications

Negative semiconductor resists such as KTFR, as described above, did not meet the resolution requirements for the semiconductor industry in the early 1970s because of swelling of the developed pattern. A new "positive" material was developed based on diazo chemistry that had been patented by Azoplate [6]. As opposed to KTFR, where the differentiation in the developing solvent between the exposed and unexposed regions relies upon a molecular weight increase in the system through cross-linking, diazo-type resists depend upon a dramatic change in polarity to achieve differential solubility. The basic resist is a two-component system where a low-molecular-weight phenolic-based resin is mixed with a diazoketone derivative. The phenolic resin provides excellent film-forming properties and is highly soluble in basic solutions. The addition of a diazonaphthoquinone photosensitizer acts as a dissolution inhibitor, and dramatically reduces the solubility of the unexposed film in basic solutions. However, upon exposure, the diazo derivative undergoes molecular rearrangement to form a carboxylic acid, and the exposed area becomes soluble in basic developers, forming a positive image. A detailed review of the chemistry of this system has been provided by a number of authors [7-9].

This positive system had a number of advantages for the growing semiconductor industry. Resolution was enhanced, since the resist was not cross-linked and did not swell in water-based developing solutions. A variety of diazoketone photoactive compounds could be engineered to optimize their absorption characteristics in the "near-UV" and "mid-UV (3130 Å)," providing extendibility to future-generation optical tools [10]. The aqueous-based developing solutions were safer and easier to use in manufacturing, and it was also found that the yield of many lithography levels, such as the device contact level, could be increased by using "dark-field" masks in conjunction with positive resists. For these reasons, positive diazo-type resists have been the backbone of the industry, and innovative chemistry was able to extend their use for a number of manufacturing applications that might otherwise have required the development of new negative resists.

For example, to fabricate high-density metal wiring for device interconnection on bipolar chips, it was necessary to convert a typical diazo resist profile [Figure 3(a)] to an "undercut" resist profile [Figure 3(b)] in order to provide a stencil for evaporated metal where the excess was removed by a "lift-off" process [Figures 3(c) and 3(d)]. This is very difficult to achieve in

positive resists, because the optical exposure dose (and hence the development rate of the system) is greater at the surface than at the resist/substrate interface, resulting in the profile seen in Figure 3(a). Conversely, a negative resist which forms more insoluble products at the resist surface than at the resist/substrate interface easily provides an "undercut" profile. However, rather than developing and implementing new negative resists in manufacturing, it was found possible to provide this profile by modifying typical diazo photoresists using a number of techniques. The first method, shown in Figure 4(a), treated the surface of a resist film with an aromatic solvent to provide a surface layer which developed at a much slower rate than the bulk resist film, providing an undercut profile during development in basic solutions [11]. Because of increasing environmental and safety concerns, this technology was replaced in manufacturing by an "image-reversal" process [Figure 4(b)]. By adding a basic molecule such as imidazole to the diazo resist formulation, it was found possible to transform a positive image that was easily removed in developer to a *negative* pattern that was resistant to basic solutions and had an undercut profile owing to the optical absorption of the system. The imidazole would react with the carboxylic acids generated upon exposure. After the film had been baked and blanket-exposed, the exposed image was less soluble in basic developers than the unexposed resist, forming a negative image which was used as a stencil in manufacturing to evaporate high-aspect-ratio metal [12-14]. However, the next-generation chips required even greater density, higher-aspect-ratio metal, and linewidth control, and it was found necessary to use reactive ion etching to form the "lift-off" pattern [15]. As shown schematically in Figure 4(c), rather than developing new resists containing silicon that would provide a photoimageable oxygen plasma etch barrier, chemists were able to modify the developed resist pattern by using a process called *silylation*. In this process, reactive monomers containing silicon functionalities are diffused into the patterned diazo-resist stencil, using an inert solvent as a carrier. These monomers react with the novolac base polymer to provide the necessary plasma etch resistance [16-18]. A silylation process is still in use today to pattern high-aspect-ratio metallurgy [19,20].

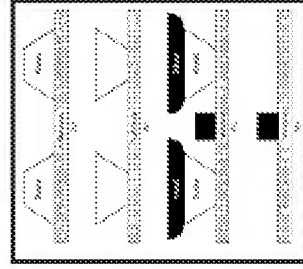


Figure 3

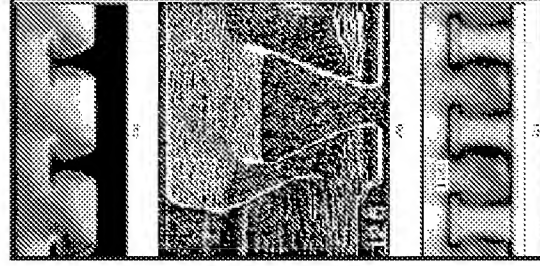


Figure 4

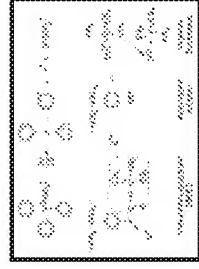
Continued development, optimization, and innovation in the materials and processing of these diazo resist systems have answered the semiconductor requirements, from the 2- μm lithography of the 1970s to current 16Mb devices with 0.5- μm ground rules. However, it was realized that continued scaling of device geometry would require new optical lithography tools utilizing the shorter wavelengths in the deep-UV (DUV) region of the spectrum ($\approx 250\text{ nm}$). In the early 1980s, research projects were initiated to develop the optical tooling and resist systems necessary for future chip generations. The first DUV projection tool, PE-500, was provided by Perkin-Elmer [21]. Because laser sources at that time were not reliable, it utilized a high-pressure mercury arc as a light source, and the output intensity was severely reduced through self-quenching of the mercury vapor. Typical diazo-type resist systems were not sensitive enough to achieve adequate manufacturing throughput, and too absorbing to achieve high resolution. Totally new resist systems had to be designed to pattern future-generation chips.

Chemically amplified negative resists

One of the most promising approaches to addressing future lithographic needs utilized discoveries in the late 1970s that photolysis of certain thermally stable onium salts [22] produced strong acids that could be used to design new photoimaging systems [23,24]. These strong acids could function as catalysts to initiate many chemical reactions, providing a path to highly sensitive resists and coatings. Compared to the conventional free-radical initiators, the onium salts have excellent thermal stability, are not sensitive to oxygen, and exhibit no "dark" or side reactions in solution. This led to the development of novel negative-resist systems in which differential solubility between the exposed and unexposed areas of the resist film was achieved by using the photogenerated acid as a catalyst to either increase the molecular weight of the system or generate chemical changes in polarity that would provide different

solubility. The increase in molecular weight could be achieved by *cationically polymerizing* monomers such as epoxies and vinyl compounds, or by enabling *condensation* reactions between phenol formaldehyde resins and amino-based cross-linkers. Changes in polarity could be achieved through the *acid-catalyzed deprotection* of a variety of esters. In addition, during this process the by-product of the deprotection regenerates the acid, hence the term *chemical amplification*. Negative resists based on all of these mechanisms have been developed; they are described in the following sections.

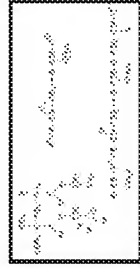
In 1982 Ito and Willson [25] reported the first "chemically amplified" resist for DUV applications based on an *acid-catalyzed deprotection* mechanism. Here, the catalytic species generated by the irradiated onium salt created many chemical changes that provided differential solubility between exposed and unexposed areas. This resulted in a change in polarity rather than an increase in molecular weight. This "gain" mechanism provided much higher quantum efficiency than typical diazo-type reactions. The first DUV negative resist system used in semiconductor manufacturing was based upon poly(4-t-butoxycarbonyloxystyrene), tBOC, and a triphenylsulfonium hexafluoroantimonate onium salt. Upon exposure in the deep UV, and subsequent baking to diffuse the photogenerated acid and complete the reaction, the acid cleaved the labile tBOC protecting groups to form a polar polyvinyl phenolic polymer, as seen in *Formula III*. The unexposed resist was removed by using a nonpolar solvent, forming a negative image. This system, known as tBOC resist, provided the exposure sensitivity required for product throughput on the DUV Perkin-Elmer tools and was used to manufacture 1Mb DRAMs in the late 1980s [26]. However, it was found difficult to control the linewidth of this new chemically amplified system in a manufacturing environment. The sensitivity of the photoresist was affected by airborne chemical contaminants. Special carbon filters had to be installed, and coatings had to be used to protect resist film from diffusion of contaminants. Also, the diffusion of the acid and hence the sensitivity and resolution of the system were found to depend upon precise control of prebake temperature, time between exposure and post-exposure bake (PEB), and the time and temperature of the PEB process itself.



Formula III

Concurrently, other resists were investigated to try to enhance the process latitude and reduce the manufacturing cost of UV resists. Epoxy materials were attractive alternatives, since there are a large variety of epoxidized polymers available in both solid and liquid form. These materials generally offer excellent adhesion to semiconductor surfaces, good sensitivity, and low cost. An epoxy derivative can be chosen to provide 1) optimum sensitivity, which is a function of the number of epoxy groups per molecule; 2) plasma resistance and thermal stability, which are functions of the backbone chemistry; and 3) resolution and contrast, which

are functions of the molecular weight and dispersivity. In 1974, Bell Laboratories had developed an electron-beam resist based on a high-molecular-weight epoxy resin, a glycidyl acrylate-ethyl acrylate copolymer shown in *Formula IV* [27]. When exposed to high-energy electron beam radiation, the material generates a reactive ionic species that subsequently reacts with an epoxy functionality to form a cross-linked system. Although it was the first resist used to fabricate optical masks, the resist properties were not adequate for fabrication of high-resolution semiconductor devices. The developer induced swelling in the pattern because of the high molecular weight of the resin. The optical sensitivity in the DUV was poor, and because the resist was based on an aliphatic backbone and contained no aromatic functionalities, the thermal stability and plasma resistance of the system were not adequate.



Formula IV

Because of the need for high-performance negative resists in the DUV, one of the first systems investigated was based on the *cationic ring-opening polymerization* of epoxy resins. Initial work on UV-curable coatings [23,24] and resist systems [28–30] demonstrated their potential. While solvent-induced swelling had degraded the resolution capability of the high-molecular-weight electron beam resists, it was hoped that this could be avoided by choosing low-molecular-weight, multifunctionalized epoxy derivatives that would form cross-linked, high-T_g films. This concurrent increase in cross-link density could not only reduce solvent swelling, but also limit the diffusion of photogenerated acid during the postexposure bake process, which can lead to linewidth degradation. Also, the substitution of epoxy functionalities on an aromatic backbone should provide thermal stability and plasma etch resistance. The first material evaluated was an orthocresol novolac glycidyl ether resin used as a chip encapsulant and commercially available from Dow as Quatex® electronic-grade materials. This multifunctional material, shown in *Formula V*, had a low molecular weight of ~4000. When formulated with a photoacid generator, this simple, low-cost epoxy photoresist (EPR) demonstrated that solvent-developable resist formulations could fabricate submicron resist patterns using the DUV PE-500 exposure tool, and reduce the dependence on bake time and temperature [31].



Formula V

Both the chemically amplified negative resist system, tBOC, and the acid-catalyzed EPR would have been capable of patterning the 1-μm ground rules required for the 1Mb chip. However, the difficulty in implementing new tooling, controlling bake processes, fabricating 1 × mask technology, and developing new resist systems had impacts on cost and scheduling. Advances in diazo resist systems, and tool improvements such as scaling the exposure wavelength and

the numerical aperture (NA) of near-UV tools, provided a more cost-effective way to fabricate semiconductor chips with gate structures down to 0.5 μm in resolution. While DUV resists would not be needed for a few more chip generations, the early experience served as an important learning vehicle. The effort to optimize these systems over the next five years led to development of the resists currently used to manufacture all CMOS logic at 0.35- μm ground rules. The APEX positive resist system is described in a companion paper [32]. The following section describes the path to obtaining a high-resolution negative resist, CGR, used to fabricate the critical structures.

High-resolution negative resists

Because of the promise shown in the first-generation epoxy DUV resist, work to improve these systems continued, and it was decided to investigate materials with high levels of epoxy functionalities in order to increase cross-linking density. Formula VI depicts a multifunctional glycidyl ether derivative of bisphenol-A novolac, available from Shell Chemical and known as EPON® resin SU-8, which provides the highest epoxy functionality commercially available. Upon exposure to either UV [33], e-beam, or X-ray radiation, it forms a ladderlike structure with a high cross-linking density and a T_g of more than 200°C. As seen in Figure 3, its versatile imaging capability has been used to fabricate advanced 0.25- μm and 0.1- μm devices using e-beam lithography [34]. The low molecular weight of the resin provides high contrast and excellent solubility and planarizing capability, and the high epoxy functionality provides sensitivity. Although the pattern is developed using a solvent, it is one of the highest-resolution systems yet developed, and it demonstrates the capability of cross-linked negative resists. It is described in greater detail in the section on micromachining.



Formula VI

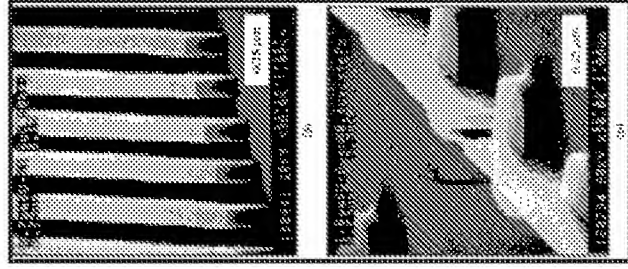
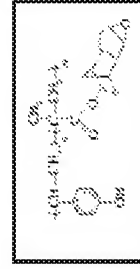
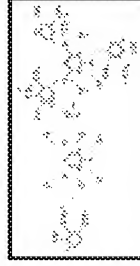


Figure 5

The first-generation cross-linked negative resists were developed using organic solvents, and it was necessary to provide new systems that could be developed in aqueous basic solutions to be compatible with diazo systems already in use, and to meet safety requirements in a manufacturing environment. An initial effort was made to blend or copolymerize cycloaliphatic epoxies with base-soluble novolacs (Formula VII). While they were base-soluble, problems due to shelf stability, difficult synthetic procedures, and residue formation made these systems difficult to implement in manufacturing. A different approach was reported by Feeley [35] at Rohm and Haas in 1986. Shown in Formula VIII, it consists of an *acid-catalyzed condensation reaction* between an aminoplast cross-linker such as a urea and melamine formaldehyde with a base-developable resin such as a novolac or poly(hydroxystyrene). These early resists had low shelf stability because the amino cross-linking agents were not stable; they were prone to self-reaction because of impurities from their industrial-scale manufacturing that were very difficult to eliminate. Also, the image stability and resolution were not adequate for the 0.35- μm lithography required for the 64Mb devices.



Formula VII



Formula VIII

Several key improvements to this basic chemistry resulted in a negative resist called CGR,

which is currently used to manufacture all critical levels of advanced CMOS logic devices [36,37]. First, it was important to control the diffusion of photogenerated acid during the post-exposure bake process. The literature indicates that diffusion of photocatalyzing acid species is critical to both resolution and dimensional control characteristics of positive, and presumably negative, resists that rely on this chemistry. In positive chemically amplified systems, the time between exposure and bake as well as the time and temperature of the PEB process must be very tightly controlled in order to ensure reproducible linewidth dimensions. However, it had previously been seen in the epoxy photoresist (EPR) that negative resists, which increase in T_g (cross-link) upon baking after exposure, provided a wider processing window with less dependence on PEB time and temperature. During the post-exposure bake of the CGR resist, the photogenerated acid cross-links the resist, which concurrently increases the T_g and decreases the polar functionalities of the system. Therefore, it was important to understand and optimize the parameters controlling acid diffusion in order to further improve the performance of the negative resist chemistry shown in *Formula VIII*. Diffusion of any species through a polymer matrix at various temperatures can be directly related to the viscosity or to other measurements of flow phenomena, such as the modulus, of that polymer. This study of flow phenomena, known as *rheological analysis*, was used for the first time to gain an understanding of acid diffusion. Rheological analysis which measures shear modulus vs. temperature, as shown in *Figure 6*, revealed that the commonly used liquid aminoplast cross-linking agents present in commercially available resists were plasticizing or softening the resist film during baking, and tended to lower the T_g of the material. The T_g of unexposed Shipley Negative Resist (SNR® 248)* is much lower than the recommended PEB of 100°C which was necessary to complete the cross-linking reaction after exposure. A new amino modifier (*Formula IX*) was identified that had a number of advantages. This new cross-linker, Powderlink® 1174 (a product of Cytek Industries, Inc.), was a solid at room temperature, with a high melting point of 90-110°C. When this modifier was incorporated in the formulation, the viscosity of the CGR at common PEB temperatures was 100 times greater than other negative systems, and, as seen in *Figure 6*, the T_g of the unexposed resist is equal to or very close to the PEB temperature. It is clear, then, that it is possible to achieve the minimum feature resolution by completing the post-exposure bake at a temperature that would provide the minimum flow or distortion (i.e., at or slightly above the T_g of the resist). Because of these improvements, the resist is less sensitive to PEB temperature conditions, so that the controls on the bake temperature are not as stringent. In addition to imparting enhanced stability during processing, the modifier eliminated the problem of resist instability during storage. Since the modifier could be purified by recrystallization, formaldehyde and acidic contaminants were easily removed, and the shelf stability problem of the photoresist solutions was eliminated.

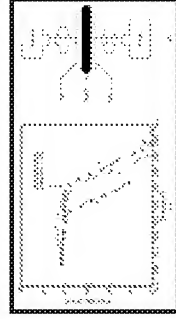


Figure 6



Formula IX

This negative-resist chemistry has a number of advantages. The resist does not require a topcoat to protect it from chemical vapors, since 1) it is less sensitive to basic contaminants because aminoplast resins already contain a tertiary amine functionality; and 2) very few reactive sites are required to turn the exposed area into an infinite cross-linked network, which dramatically increases differential solubility. Before the post-exposure bake, the resist has a T_g similar to the recommended PEB temperature of 100°C , which serves to control the initial diffusion and distortion. During the PEB cycle, diffusion can be further reduced, as the resist increases in T_g and the polar functionalities which may serve as diffusion paths [38] are decreasing. Also, because the exposed image is cross-linked, there is less dependence on developer time and temperature conditions, and the exposed image can be overdeveloped without affecting linewidth dimensions.

The combination of the enhanced processing properties of CGR, its excellent resolution capability, and the ability to use a dark-field mask to reduce reflections in the lens and resist [39,40] has led to tighter control of the linewidth across the chip. As shown in Reference [41, Figure 13], this tight control of the channel length is critical to achieving device performance and yield [41-43]. Reference [41, Figure 15(a)] compares the linewidth control that can be achieved with APEX, a positive resist, where isolated lines are 8% larger than nested lines, and that of a negative CGR resist [41, Figure 15(b)], where the isolated and grouped lines print at the same dimension. This negative resist is currently being used in the fabrication of all 0.35- μm CMOS devices and is commercially available from the IBM/Shibley Deep-UV Resist Alliance. The excellent resolution of an advanced version of CGR is shown in Figure 7, where 200-nm resolution has been achieved using a Micrascan@ 248-nm exposure tool with 0.5 NA.

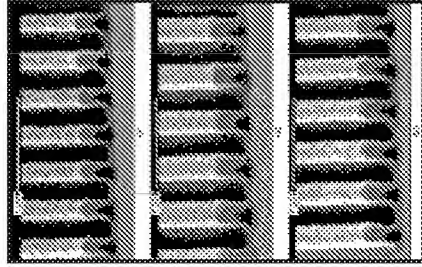


Figure 7

While the differential solubility in CGR is achieved through a cross-linking reaction, new chemistry approaches to acid-catalyzed "deprotection" may lead to interesting negative-resist systems [44].

3. Negative resists for micromachining applications

The ability to machine small parts using silicon etching or pattern electroplating is of growing interest in the electronics industry, where it can be applied to the future miniaturization of magnetic disk drives, electron-beam columns, semiconductor test probes, sensors, waveguides for optical networks, and field-emission tips and light modulators for display technologies. Many of these applications require high-aspect-ratio lithography (thickness/resolution) using thick resist films (>50 µm) to provide stencils with excellent dimensional control and vertical sidewalls. The best-known technique for forming these high-aspect-ratio structures is a LIGA (Lithographie, Galvano-formung, Abformung) process [45] in which a thick film (up to 1 mm) of PMMA is patterned using a synchrotron X-ray source. Since this is an expensive, time-consuming process with limited exposure tool availability, it would be desirable if possible to use optical lithography tools and associated commercially available photoresists. Recently several authors have reported on the use of negative photosensitive PWB resists and polyimides [46, 47] and positive diazo-type photoresists [48-51]. While these systems are useful for some applications, it is generally difficult to achieve high-aspect-ratio patterns because of 1) the resolution limitations of thick PWB resists, 2) the high optical absorption of typical semiconductor resist systems, and 3) the difficulty in producing coatings thicker than 50 µm. New resist systems designed specifically for micromachining applications are required which can be spin-coated to achieve thick films that have excellent sensitivity, high resolution, low optical absorption, thermal stability, and chemical resistance.

Epoxy materials are attractive candidates for this application because they are available in a wide variety of molecular weights at low cost. As stated previously, work in the early 1980s reported that epoxy resins could be cationically polymerized by using a photoinitiator such as an onium salt, which generated a strong acid upon exposure to ultraviolet light [24].

One material that looked very promising for this micromachining application [52, 53] was a multifunctional epoxy derivative of a bis-phenol-A novolac (SU-8), which had previously been used to provide the high-resolution patterning for semiconductor devices described in a previous section. This material has the highest epoxide functionality commercially available (Formula VI); when formulated with a commercially available triaryl sulfonium salt as photoinitiator (CYRACURE® UVI from Union Carbide), coated on a substrate, and exposed to ultraviolet light (365 to 436 nm), the epoxy resist will form a highly structured cross-linked matrix. In addition to the exposure sensitivity and the excellent adhesion of epoxy derivatives, this resist system has three important attributes which make it very suitable for thick-film applications. First, because of its low molecular weight of ~7000 (±1000), SU-8 can be dissolved in a variety of organic solvents such as propylene glycol methyl ether acetate (PGMEA), gamma-butyrolactone (GBL), or methyl iso-butyl ketone (MIBK) to provide solutions

containing up to 85% solids by weight. Thicknesses of 200 μm can be obtained with a single spin-coating. Second, this material has a very low optical absorption in the near-UV; *Figure 8* compares the optical absorption of SU-8 with a typical diazo-type resist system and a dry-film RISTON® resist system from DuPont. Owing to this high transparency, aspect ratios of 14:1 have easily been obtained [54], as seen in the scanning electron micrograph in *Figure 9*. Third, because of its aromatic functionality and highly cross-linked matrix, the exposed resist is thermally and chemically stable, making it more suitable for the prolonged plasma etching and electroplating processes than PMMA materials. *Figure 10* shows the thermal stability of the patterned structures.



Figure 8

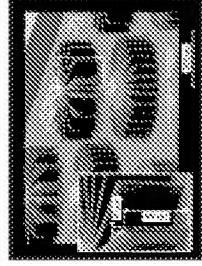


Figure 9



Figure 10

This system has been used to fabricate a variety of high-aspect-ratio microstructures for microelectromechanical (MEM) applications. To fabricate an advanced IBM electron-beam microcolumn [55], miniature octupole lenses are required to deflect and scan the electron beam. Both silicon and gold micro-octupoles were fabricated by using the high-aspect-ratio SU-8 structures as a plasma-resistant stencil to etch silicon, and as a plating mask to electroplate gold [56]. Also, another recent application has been in the fabrication of micromotors [57].

For certain MEM applications, the use of SU-8 resist provides a low-cost, easily implemented alternative to the LIGA process. While the film thicknesses are currently limited to 200 μm , near-UV patterning of up to 500 μm is anticipated in the near future. Also, the solvents used to strip the SU-8 stencil are not always compatible with the composition of the substrate, and research is continuing to provide high-resolution negative systems that are more easily removed.

Conclusions

Tremendous advances have been made in the development of negative-resist systems since they were introduced in the early 1960s. Their sensitivity, ease of chemical modification, and low cost have made them the materials of choice for the PWB industry; and they are being continually improved to provide greater resolution, ease of processing, and improved physical and thermal properties. For the semiconductor industry, it has been necessary to provide

negative resists to meet the ever-increasing circuit density requirements for every new generation of semiconductor devices. Improvements in cross-linked resists have eliminated the swelling seen in early resist systems, and have provided the highest-resolution systems to date. Currently, negative resists based on acid-catalyzed cross-linking are used to fabricate the critical 0.35- μm level of advanced CMOS chips, where linewidth control is key to performance. This is due both to the wider processing latitude of the resist and to the ability to pattern this critical level using a dark-field mask to reduce scattered light reflections in the optical exposure tool lens and in the resist film itself. Work is in progress, both to improve similar systems and to provide new chemistry choices, since the many lithographically patterned levels of circuitry may require both positive and negative systems. Future 193-nm optical exposure tools are currently under development to provide devices with gate widths smaller than 0.2 μm . Current resist systems are too optically absorbing at 193 nm, so incremental improvements in these systems will not achieve future resolution requirements. Totally new resist chemistry and processes must be developed.

Acknowledgment

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References

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